"On the Capacity for Heat of Water between the Freezing and
Boiling Points, together with a Determination of the
Mechanical Equivalent of Heat in Terms of the International
Electrical Units.—Experiments by the Continuous-flow
Method of Calorimetry performed in the Macdonald Physical
Laboratory of McGill University, Montreal." By HOWARD
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cated by Professor H. L. CALLENDAR, F.R.S. Received June
15,—Read June 21, 1900.

(Abstract.)

At the Toronto meeting of the British Association in 1897, a new
method of calorimetry was proposed by Professor Callendar and the
author for the determination of the specific heat of a liquid in terms
of the international electrical units. At the Dover meeting in
September, 1899, some of the general results obtained with the
method for water over a part of the range between 0° and 100°
were communicated, with a general discussion of the bearing of the
experiments to the work of other observers. In the present paper
the author gives a summary of the complete work, in the case of water,
to determine the thermal capacity at different temperatures between
the freezing and boiling points.

Theory of the Method.

If a continuous flow of liquid in a tube be made to carry off a con-
tinuously supplied quantity of heat EC, in electrical units, then after
all temperature conditions have become steady

$$JsQ(\theta_1 - \theta_0)t + (\theta_1 - \theta_0)ht = ECt$$

where

J = mechanical equivalent of heat,
Q = flow of liquid per second,
s = the specific heat of the liquid,
θ_0 = the temperature of the liquid flowing into the tube,
θ_1 = the temperature of the liquid flowing out of the tube,
h = the heat loss per degree rise of temperature from the liquid
    flowing through,
t = the time of flow.

In the case of water, E represents the E.M.F. across an electrical
heating conductor in the tube, and C the current flowing. In this
case, which is treated of entirely in the present paper, Js is replaced

by 4·2 $(1 \pm \delta)$ where δ is a small quantity to be determined, and varies with the thermal capacity of the water, which is not exactly equal to 4·2 joules at all points of the range.

Substituting in the general equation, rearranging terms, and dividing through by t, the equation is given in the following form :—

$$4 \cdot 2 Q(\theta_1 - \theta_0)\delta + (\theta_1 - \theta_0)h = EC - 4 \cdot 2 Q(\theta_1 - \theta_0),$$

which is termed the general difference equation of the method. The two terms δ and h may be determined by using two values of Q, giving two equations of the form

$$4 \cdot 2 Q_1(\theta_1 + \theta_0)\delta_1 + (\theta_1 - \theta_0)h = E_1 C_1 - 4 \cdot 2 Q_1(\theta_1 - \theta_0)$$

$$4 \cdot 2 Q_2(\theta_2 - \theta_0)\delta_2 + (\theta_2 - \theta_0)h = E_2 C_2 - 4 \cdot 2 Q_2(\theta_2 - \theta_0).$$

For the same value of θ_0, if the electrical supply for the two flows is regulated so that $\theta_1 = \theta_2$, then $\delta_1 = \delta_2 = \delta$, and by eliminating h,

$$\delta = \frac{(E_1 C_1 - 4 \cdot 2 Q_1(\theta_1 - \theta_0)) - (E_2 C_2 - 4 \cdot 2 Q_2(\theta_1 - \theta_0))}{4 \cdot 2 (Q_1 - Q_2)(\theta_1 - \theta_0)}$$

which corresponds to the mean temperature

$$\theta_0 + \frac{\theta_1 - \theta_0}{2},$$

where $(\theta_1 - \theta_0)$ is not too great.

In the present method the flow tube is of glass, about 2 mm. in diameter, connected to two larger tubes forming an inflow and an outflow tube, in which the temperature of the water is read, by a differential pair of platinum thermometers, before and after being heated by the electric current. A glass vacuum jacket surrounds the fine flow tube and a part of the inflow and outflow tubes, to reduce the heat loss as much as possible. A copper water jacket encloses the inflow tubes and vacuum jacket, in order to maintain the glass surface of the vacuum jacket always at a constant temperature equal to the inflowing water. The heat loss from the water is then the loss due to radiation from the flow tube through the vacuum jacket, and conduction from the ends of the flow tubes.

In testing the accuracy of the method, the dependence of the heat loss on the rise of temperature was found, and the dependence of the heat loss on the flow.

Measurement of Fundamental Constants.

The electric heating current supplied to the wire conductor in the fine-flow tube was taken from four large 200-ampere hour accumulators. It was passed through a standardised resistance in series with the wire

conductor and in addition a specially constructed rheostat, by which small adjustments to the circuit could be made for regulating the heat supply.

The measurement of the different constants entering into the general difference equation of the method is treated of under two heads, Electrical and Thermal. In the first, the Clark cell and resistance form the principal measurements, and in the second the measurement of temperature, time, and weight have to be considered. An exceedingly accurate potentiometer was employed to determine the difference of potential across the resistance and calorimeter in terms of the E.M.F. of the Clark cell.

Experimental Proof of the Theory of the Method.

In this section the author shows that the dependence of the heat loss per degree rise in the calorimeter varies in a linear relation to the flow in proportion to $4\cdot2\,Q\delta$ beyond certain limits of flow, and that this is essential for the fulfilment of the theory of the method. For very small flows the conduction effect at the outflow end, due to the rise of temperature in the water, appears and causes the line representing the relation of heat loss to flow to approach an infinitely large value of the heat loss for a zero flow. The limits of flow chosen in the present measurements are safely included within the linear relation.

The relation of the heat loss to the rise of temperature shows that for rises of from 2° to 8° and beyond, the heat loss is directly proportional to the rise. The thermal capacity of the calorimeter is calculated, and it is shown that for the small changes in the temperature of the calorimeter during an experiment this is negligible.

Effect of Stream-line Motion.

Some of the earlier results are given in this section, showing the effect of stream-line motion on the distribution of heat throughout the water column for a calorimeter with a 3-mm.-bore flow tube for different flows. The temperature of the heating wire used for these experiments is also calculated, and found to vary considerably when moved from the centre to the sides of the tube. It was found necessary to thoroughly stir the water in its passage through the flow tube, in order to ensure a perfectly uniform temperature throughout the water column.

Preliminary Measurements.

The preliminary measurements of the value of J, which were made in the summer of 1898, were affected by the presence of stream-line motion in the tube, as at that time no device was introduced to

obviate it. Owing to the calorimeter which was used then, however, having only a 2 mm.-bore flow tube, the effect was not so large as for the tube with a 3 mm. bore. The value which corresponds to a temperature of the water of 30° C. is 4·1805 joules, which agrees to 1 part in 2000 with the later and more accurate measurements which were obtained for all the calorimeters with the various devices for eliminating the stream-lines.

Experiments between 0° *and* 100°.

In this section the complete list of fifty-five tables is included, giving upwards of forty-five complete experiments at different parts of the range. The experiments have extended over just a year, and divide themselves naturally into eight separate series. The results with different calorimeters and with different rises of temperature are included. Summarising the results and plotting the values of δ for all the experiments, the following values of δ and the corresponding values of J are obtained from the smoothed curve :—

Summary of the Specific Heat of Water from Smoothed Curve.

Temperature. °C.	δ.	J.
5	+ 0·00250	4·2105
10	− 0·00050	4·1979
15	− 0·00250	4·1895
20	− 0·00385	4·1838
25	− 0·00474	4·1801
30	− 0·00523	4·1780
35	− 0·00545	4·1773
40	− 0·00545	4·1773
45	− 0·00520	4·1782
50	− 0·00480	4·1798
55	− 0·00430	4·1819
60	− 0·00370	4·1845
65	− 0·00310	4·1870
70	− 0·00245	4·1898
75	− 0·00180	4·1925
80	− 0·00114	4·1954
85	− 0·00043	4·1982
90	+ 0·00025	4·2010
95	+ 0·00090	4·2038

Mean value .... 4·18876

The values of δ represent the specific heat of water in terms of a thermal unit equal to 4·2000 joules, which occurs at 9° C. It is more

suitable to select a thermal unit at a more convenient part of the scale. The mean value of the mechanical equivalent of heat from these measurements over the whole range is 4·18876 joules, which is very nearly equal to the value at 16° C., which is 4·1883 joules. It seems desirable to select a unit at a temperature which, if at the same time at a convenient part of the scale, may be equal to the mean value over the whole scale. The author has in consequence adopted a unit at 16° C., and has expressed the specific heat of water in the following table in terms of this unit :—

Variation of the Specific Heat of Water in Terms of a Thermal Unit
at 16° C.

Temperature. ° C.	Observed values.	Calculated values.
5	1·00530	1·00446
10	1·00230	1·00206
15	1·00030	1·00024
20	0·99895	0·99894
25	0·99806	0·99807
30	0·99759	0·99757
35	0·99735	0·99735
40	0·99735	0·99735
45	0·99760	0·99757
50	0·99800	0·99807
55	0·99850	0·99894
60	0·99910	0·99910
65	0·99970	0·99972
70	1·00035	1·00036
75	1·00100	1·00100
80	1·00166	1·00166
85	1·00237	1·00233
90	1·00305	1·00301
95	1·00370	1·00370

Mean...... 1·00012

In expressing the results in a formula it is impossible to fit any one simple expression over the whole scale. It is seen that the curve falls rapidly from 0°, passes through a minimum point at 37·5°, and increases again less rapidly towards 100°. Two formulæ can be fitted very accurately over the scale. Between 5° and 37·5° C. the following expression in terms of a thermal unit at 16° is found to read,

$$S = 0·99733 + 0·0000035 (37·5 - t)^2 + 0·00000010 (37·5 - t)^3.$$

The same formula holds between 37·5° and 55° by simply consider-

ing all values of the cubical term positive. Above 55° the simple formula

$$S = 0.99850 + 0.000120\,(t - 55°) + 0.00000025\,(t - 55)^2$$

holds with great accuracy.

Both these formulæ are given for comparison in the second table. They fit very closely except below 5°, where the specific heat curve increases more rapidly. These lower values are within 1 part in 1000, however.

A summary of the values obtained for the radiation loss shows that the absolute value for any one calorimeter cannot be relied on to an order of accuracy greater than 1 part in 1000 over extended periods. This is particularly true when the temperature of the calorimeter is widely changed. It was found most essential to always eliminate the heat loss from at least two different flows in order to be completely independent of its absolute value. The complete independence of the results from the value of the heat loss, provided this remained constant throughout the time of an experiment, was shown by employing calorimeters with different degrees of vacuum involving widely differing values of the heat loss. The temperature coefficient of the radiation loss was found to be almost exactly linear over the range of these experiments.

Relation to the Work of other Observers.

It is at once apparent that the value of the mean mechanical equivalent of heat obtained from these measurements, which is 4·18876 joules, is somewhat larger than the exceedingly accurate and trustworthy measurements of Reynolds and Moorby. Their value, which is 4·18320 joules, is lower by 0·132 per cent., or a little over 1 part in 1000.

It is evident that this error may be attributed to the neglecting of some correction factor in the present series of experiments at the extremities of the range, which would cause the variation curve to increase more rapidly than it truly does; but from the order of accuracy with which the theory of the present experiments holds at the extremities of the range, it is far more likely that the variation curve is correct, and that the difference in the two results is to be attributed to an error in one of the constants. The thermal constants employed in the two different experiments are referred to the same values, but the introduction of the value of the electrical units into the present series of experiments, which do not enter into the calculation of Reynolds's and Moorby's result, renders it highly probable that the error is to be looked for here. In view of the immense amount of labour expended in establishing the value of the inter-

national ohm, it is probable that the error is not there. The recent work on the absolute value of the Clark cell, which is demanding so much attention just now, and which has so far given so many inconsistent results, makes it very probable that the value of the Clark cell adopted in the present work is in error. If this is so, then, as is pointed out, the value of the Clark cell must be taken as 1·43325 int. volts at 15° C., in order to bring the present series of experiments, involving both the international volt and ohm, into absolute accord with the result by the direct mechanical method of Reynolds and Moorby.

Having considered the above relationship, the mean value of the mechanical equivalent given by Rowland's experiments between 6° and 36° C. is compared with the same mean value from the present series of experiments over the same range. By expressing this latter value in terms of the value of the Clark cell 1·43325 volts, or as may be said in terms of Reynolds's and Moorby's determination, instead of the original value 1·43420 volts used in calculation, it comes equal to 4·1817 joules. The value obtained from Rowland's corrected curve is 4·1834 joules, which agrees with the present series of experiments to 1 part in 2000. This is a discrepancy so small as to be, if not within the limits of error of these several determinations, at least negligibly small in comparison to the great range covered by the present series of experiments.

By far the most difficult part of the present series of experiments is the comparison of the absolute value of the mechanical equivalent of heat obtained from these experiments with the values obtained by the electrical method used by Griffiths, and by Schuster and Gannon, even when our several results are expressed in terms of the same values of the units used. There is every reason to believe that the values of the resistance standards used in the present work were the same as those used by both these investigators. It is also highly probable that the values of the Clark cells in the present series of experiments were in correct agreement with all the best results that have been obtained in setting up this electro-chemical combination. It is probable that the difference in the values obtained by Griffiths, and by Schuster and Gannon, from the value obtained in the present series of experiments must be attributed not to these, but to the radical difference in the methods of calorimetry.